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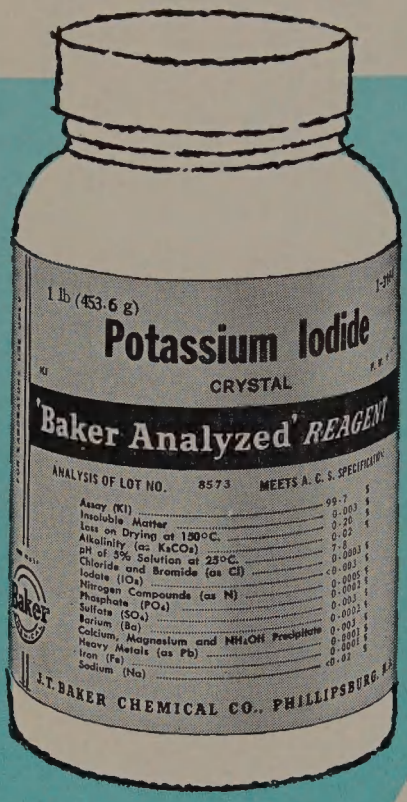
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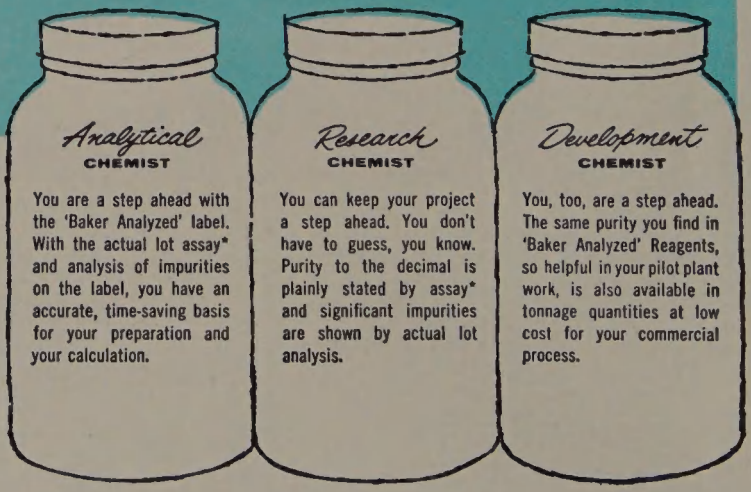
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REVIEW

Thioacetamide in Analytical Chemistry

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It is the ideal of analytical chemistry to have a series of reactions for the detection and determination of each ion in the presence of all others. However, it is questionable if such reactions will be found for all ions. As a result, it is necessary to effect preliminary separation of ions into groups and thereby to reduce possible interferences in many specific tests. For more than a century, hydrogen sulfide has been used routinely for both qualitative and quantitative group separations because of the insolubility of the sulfides of most cations and because of the many procedures based on the behavior of such sulfides. However, there are many disadvantages to the use of hydrogen sulfide, including its toxicity and its nauseating odor.

Over the years, research has been directed toward finding a satisfactory substitute for hydrogen sulfide, including the study of inorganic and organic sulfur compounds which decompose in solution to give hydrogen sulfide (*e.g.,* thiourea, thiosulfates, thioacetates, thioglycollates, thiosalicylates, and thiocarbonates). However, only one of these compounds has shown itself to be of general, practical use — thioacetamide.

Thioacetamide as a Sulfide Precipitant

Thioacetamide hydrolyzes smoothly in acid or alkaline solution to give hydrogen sulfide. Since its use is very similar to that of hydrogen sulfide without the disadvantages of the latter, there is no need for the development of radically new procedures, and the experience gained from the use of hydrogen sulfide gas is directly applicable.

However, the use of thioacetamide presents so many more advantages that it is more than a mere substitute for hydrogen sulfide. Precipitates obtained by the use of thioacetamide, in contrast with those with hydrogen sulfide, are coarsely crystalline, dense, easily filterable, and less contaminated with foreign ions. Further, by controlling the temperature of the thioacetamide solution, the rate of hydrolysis can be controlled and thereby the rate of precipitation of sulfides can be regulated. No special arrangements are required for the use of thioacetamide, such as gas generators or delivery tubes. Further, loss of small quantities of precipitates which adhere to glass tubes is avoided. Because cations can be precipitated by nearly stoichiometric amounts of thioacetamide, there is seldom need to perform such operations in a hood.

Properties of Thioacetamide

Thioacetamide forms well-defined white crystals and has been variously reported to melt at 107 to 115°C. It is very soluble in water, alcohol, and benzene, and its neutral aqueous solution is stable for months. Although thioacetamide solutions develop a slight turbidity when stored for long periods of time, the performance of the reagent is not affected and the solutions may be used after filtration.

In solution, thioacetamide is undoubtedly an equilibrium mixture of the amide and its enol:

$$CH_3CSNH_2 \rightleftharpoons CH_3C(SH)=NH$$

The hydrolysis of thioacetamide takes place in either acidic or alkaline solution, slowly in the cold but more rapidly with increasing temperature. It is also affected by the concentration of acid or alkali. The equations for the hydrolyses are:

$$\text{Acid: } CH_3CSNH_2 + 2H_2O = CH_3COONH_4 + H_2S$$

$$\text{Base: } CH_3CSNH_2 + 3OH^- = CH_3COO^- + NH_3 + S^{-2}$$

Early Use of Thioacetamide

The use of thioacetamide as a general analytical reagent was first reported by Iwanov (*1*) in 1935 for the detection of heavy metals in pharmaceutical preparations. Vavilov (*2*) used an alcoholic solution of thioacetamide as a nearly specific reagent for the detection of bismuth in the presence of the other metals of the same analytical group through the formation of a yellow coloration, presumably $BiO(SCNHCH_3)$.

The possibility of replacing gaseous hydrogen sulfide with thioacetamide in qualitative procedures was first mentioned in 1949 by Barber and Grzeskowiak in a short note (*3*). In 1951, a complete scheme of analysis using thioacetamide was published by Lipiec and Pryszczewska (*4*). The results of further investigations of the use of thioacetamide in qualitative procedures have been revealed in a series of texts on qualitative analysis, the first of which was by Barber and Taylor (*5*).

Thioacetamide in Qualitative Analysis

In general, qualitative procedures using thioacetamide are fundamentally identical with those using hydrogen sulfide and differ only in manipulative details. However, it is necessary to adhere to the specified concentration of acid or base, temperature, and time of heating in order to assure success. The published procedures differ in the preparation of the sample for the separation of group II and III cations.

Adjusting Acidity for Group II

After the separation of group I chlorides, the filtrate containing groups II to V may be adjusted to the proper acidity for the precipitation of group II in any of the following ways:

(*a*) Evaporate the filtrate almost to dryness, add 0.25 ml. of one normal hydrochloric acid and dilute to 1 ml.

(*b*) Add a drop of 0.02 per cent malachite green solution and adjust to a blue-green color by adding dilute aqueous ammonia or hydrochloric acid. Then add 1 drop of 0.05 per cent alcoholic solution of thymol blue and add hydrochloric acid until the solution appears reddish against a white background. This solution will be two-tenths normal in hydrogen ion and the sulfide precipitates obtained from it may not have their proper colors owing to adsorption of the indicators (*5*).

(*c*) Add 1 drop of 2,4-dinitrophenol indicator (0.175 g. with 4 ml. of 0.1 *N* sodium hydroxide in 250 ml. of water) and then add aqueous ammonia until the solution is yellow. Now add dilute hydrochloric acid dropwise until the solution is colorless (pH = 3); for each milliliter of the solution add 4 - 5 drops of one normal hydrochloric acid.

(d) Evaporate the solution almost to dryness and take up the residue in 0.3 *N* hydrochloric acid.

Separation of Group II

After the acidity has been adjusted by any of the above procedures, the cations of group II may be precipitated in the following way and subsequently treated according to the usual semimicro qualitative schemes (*5,6*):

Add 5 drops of 5 per cent thioacetamide solution and heat in a water bath for at least 5 minutes, add 2 - 3 ml. of water and then heat for at least 2 minutes longer. Filter and wash with water containing one drop of one normal hydrochloric acid per ml. (*5*).

Alternatively, the separation of group II may be effected as follows: Make the filtrate from group I two normal in hydrochloric acid; add excess 2 per cent thioacetamide solution and heat in a boiling water bath 5 minutes. Then, adjust the acidity to pH 0.5 by diluting until a drop of the solution gives a yellow color with a drop of the indicator made by mixing 0.3 gram hematoxylin with 0.06 gram methyl violet B and dissolving in a mixture of 20 ml. of water and 80 ml. of isopropanol. Finally, heat the solution 2 minutes, filter, and wash the precipitate (*6*).

Separation of Group III

After the removal of group II cations as their sulfides, the filtrate may be treated for the separation of group III cations by thioacetamide in one of the following ways:

(*a*) Heat the filtrate to boiling and add 3 - 4 drops of concentrated aqueous ammonia mixing well after each addition to promote coagulation of the precipitate. Filter and wash the precipitate with about one ml. of water (*5*).

(*b*) Make the filtrate two normal in hydrochloric acid and add more thioacetamide. Heat for 3 minutes in a boiling water bath and make the solution ammoniacal. Continue heating for 10 minutes, filter and wash the precipitate as usual (*6*).

(*c*) Destroy the residual thioacetamide from the group II precipitation by adding and boiling with a few drops of concentrated nitric acid (*6*). Remove sulfur and precipitate iron, aluminum, and chromium with ammonia. Filter and wash the hydrous oxides; add thioacetamide to the filtrate and proceed as above in (*a*) or (*b*).

Remarks

The rate of formation of sulfides depends on the conditions in solution and on the metal ions. There are great differences in the rates of precipitation of the cations, and they are especially pronounced in cold solutions. For example, lead sulfide can be precipitated almost instantaneously by thioacetamide in ammoniacal solution but zinc sulfide precipitates only very slowly under these conditions. This fact permits the detection of lead in zinc oxide pigments (*7*):

Detection of Pb in ZnO

Depending on the lead content, dissolve 5 - 500 mg. of zinc oxide pigment in 2 - 3 drops of dilute hydrochloric acid. Then add an excess of concentrated aqueous ammonia to the cold solution together with 4 - 5 drops of 2 per cent thioacetamide solution. If lead is present, a brown coloration occurs at once and some minutes later, white zinc sulfide will form. With experience, the lead content can be estimated by the extent of the coloration and the amount of sample.

Thioacetamide in Quantitative Procedures

The use of thioacetamide in quantitative analysis was first studied by Flaschka and co-workers (*8, 9, 11*). It was to be expected that the coarser precipitates formed by thioacetamide would be less contaminated by foreign ions, easier to filter, and therefore more suitable for gravimetric analyses than those formed by hydrogen sulfide. This was found to be true for some metals.

For nine metals of group II, Flaschka and Jakoblejewich (*8*) found that the precipitation conditions must be strictly maintained over a limited range of acidity in order to make it possible to weigh the precipitates. In many instances it was found that the weight of metal sulfide obtained with thioacetamide is consistently high but that by application of a correction factor, adequate results could be obtained. Occasionally, some cations form lightly colored addition compounds or salts with thioacetamide but these give way to the sulfide.

Thioacetamide procedures yield sulfides quickly and more expeditiously than do procedures using hydrogen sulfide. The combination of thioacetamide precipitations with titrimetric methods offers savings of time and elimination of the tedious preparations needed for passing hydrogen sulfide gas into solutions. When thioacetamide precipitations are used together with a universal titrant such as ethylenediaminetetraacetic acid (EDTA) a great many tedious analyses are simplified and greatly shortened. For example, the iodometric titration of copper (*8*) and the bromate titration of antimony (*8*) are shortened considerably by a preliminary separation with thioacetamide. The determination of nickel or cobalt with the combination of EDTA and thioacetamide (*11*) serves as another example.

Table I summarizes gravimetric procedures applicable to 25 to 500 mg. of some metals as found by Flaschka and co-workers (*8, 9, 11*). For working details, the original papers should be consulted. In Table I the "maximum normality of acid" refers to the optimum conditions that yield sulfides suitable for weighing and it is *not* to be inferred that quantitative *separations* are impossible at other acidities. These procedures can also be applied to microamounts of metals. For example, Flaschka (*13*) has reported microprocedures for mercury, bismuth and arsenic.

It should be emphasized that sulfide precipitation by thioacetamide is in general of more value as a preliminary separation step than as a direct gravimetric procedure.

For some cations, precipitation may be incomplete if only small amounts are present. For example, the precipitation of manganese by thioacetamide will be quantitative so long as more than 5 mg. of the metal are present in 100 ml. of solution (*9*). Of course, small quantities of manganese can be determined by adding enough standard manganous sulfate solution to exceed the critical value of 5 mg. of manganese per 100 ml.

Pohl (*16*) has analyzed spectroscopically the trace impurities in high purity aluminum by employing thallous sulfide as a trace carrier. Thioacetamide was used for the sulfide precipitation from the nitric acid solution of the aluminum sample.

Sulfide precipitates obtained from thioacetamide are not as adsorptive as those obtained from hydrogen sulfide. Even small quantities of the alkaline earths can be determined accurately in residual solutions after separation of uncontaminated metal sulfides by thioacetamide (*9*).

TABLE I. QUANTITATIVE PRECIPITATIONS WITH THIOACETAMIDE

Metal	Max. normality of acid HCl	H_2SO_4	NHO_3	Dry at	Approx. % error (±)	Note
Mercury	0.2	0.5	0.5	110° C.	0.3	a
Copper	2	6	0.5	———	———	b
Bismuth	1	——	2	280° C.	0.2	c
Cadmium	1	6	—	———	———	d
Lead	0.1	——	0.3	350° C.	———	e
Arsenic (III)	1	6	1	110° C.	0.3	f
Arsenic (V)	6	6	—	105° C.	0.3	
Antimony (III)	1	——	—	110° C.	1.0	g
Antimony (III, V)	3	——	—	290° C.	0.1	h
Tin	1	——	—	(incomplete precipitation)		i
Germanium	—	6	—	(ignition to GeO_2)		j

(*a*) HgS pptd. with thioacetamide by Volhard procedure (*15*) not suited for weighing. (*b*) CuS pptd. by thioacetamide can not be weighed directly. (*c*) Dry and cool under CO_2; from ammoniacal solution, results high. (*d*) CdS pptd. in presence of NH_4 salts, fumed with H_2SO_4, weighed as $CdSO_4$. (*e*) Pptn. by 5-fold excess of thioacetamide; PbS dried in CO_2. (*f*) Results usually 0.6 % high and must be corrected. (*g*) These conditions yield red sulfide. If dried in CO_2 at 290° C., results 0.5 % low and must be corrected. (*h*) Black sulfide formed quantitatively. By drying at 290° C. in CO_2 stream, Sb_2S_5 converted to Sb_2S_3. (*i*) See original reference (*8*). By adding Hg^{+2} to solution, Sn can be recovered quantitatively. (*j*) Bartelmus & Hecht (*10*) have used HCl soln, but chloride is volatile.

Thioacetamide—EDTA Separations

The combination of thioacetamide with ethylenediaminetetraacetic acid (EDTA) offers new possibilities for separations because the EDTA prevents the precipitation of some metals as their sulfides. Preliminary studies of such combinations have been published by Flaschka (*14*). Among the results obtained from these studies is the interesting fact that the equilibrium of the metal-EDTA-thioacetamide system can be shifted by the addition of calcium ion. Thus, metals can be separated as sulfides by precipitating some of them with thioacetamide in EDTA solution and then precipitating the remainder by the addition of a large amount of calcium ion to the filtrate.

The following paragraphs summarize the characteristics of the thioacetamide precipitation of some metals especially as to the effect of EDTA (*14*).

Silver. Thioacetamide precipitates Ag_2S at once in the cold from ammoniacal or neutral solutions. In the presence of small quantities of nitric acid, sulfur forms first and then the silver sulfide deposits. In sulfuric acid solution, the sulfide is precipitated only upon heating. EDTA does not prevent the formation of Ag_2S.

Thallium (*1*). In the cold, thioacetamide does not precipitate thallous salts from neutral

or acetic acid solution, and only a slight reddish turbidity is formed after boiling 5 - 10 minutes. On the other hand, the sulfide is precipitated immediately from ammoniacal solution even in the presence of EDTA.

Thallium (III). A slightly acidic, cold solution of thallic salts containing thioacetamide forms Tl_2S after addition of ammonia. The reaction can be masked by EDTA and demasked by calcium ions.

Mercury (II). In ammoniacal or alkaline solutions, the reactions of mercuric ions with hydroxyl ions or ammonia are masked by EDTA, but thioacetamide precipitates black HgS even in the cold.

Copper. Although EDTA in ammoniacal solution does not prevent the precipitation of CuS by thioacetamide, the rate of precipitation is influenced by the concentration of the complexing agent, and the formation of CuS requires prolonged boiling in order to be complete. However, the addition of calcium precipitates CuS at once.

Bismuth. Brown bismuth sulfide is precipitated by thioacetamide from cold or warm ammoniacal solutions containing tartrate or EDTA.

Cadmium. Neutral solutions of cadmium salts yield a faint turbidity with thioacetamide after boiling for a long time, but complete precipitation will occur after prolonged boiling in acetic acid or potassium cyanide solutions containing large amounts of thioacetamide. A high concentration of EDTA in ammoniacal solution delays and even prevents the precipitation of CdS, but calcium ions in excess cause immediate precipitation. EDTA solutions made alkaline with sodium hydroxide precipitate CdS slowly in the cold, more rapidly when heated.

Lead. Thioacetamide slowly precipitates coarsely crystalline PbS from hot, neutral or weakly acid solutions, but the precipitation is extremely rapid from a solution initially acid and then made ammoniacal. EDTA does not mask lead.

Arsenic. EDTA does not prevent the complete precipitation of As_2S_3 from strongly or weakly mineral acid solutions. In acetic acid solution, arsenic is incompletely precipitated, even on prolonged boiling.

Tin (II). The brown SnS is formed by heating ammoniacal tartrate solutions with thioacetamide; EDTA prevents the precipitation, and calcium ions permit the formation of SnS in its presence. A nearly black precipitate is formed from hot or cold stannite solutions.

Tin (IV). The yellow SnS_2 precipitates from ammoniacal tartrate solutions; the presence of EDTA does not influence the formation of the precipitate.

Zinc. Only a slight turbidity results from the boiling of neutral or weakly acidic (mineral or acetic) solutions of thioacetamide and zinc salts. A difficultly filterable precipitate of ZnS forms in hot ammoniacal solution. However, if the ammoniacal solution is allowed to remain cold for 1/2 to 3/4 hour and then heated, a very dense, easily filterable and washable precipitate forms after a long incubation period. The rate of precipitation is accelerated by the presence of ZnS particles and is much higher in solutions containing sodium hydroxide.

Iron. Ferric solutions (acid) are reduced by thioacetamide and become turbid from sulfur. The addition of ammonia immediately leads to the formation of black FeS. A very coarse sulfide is formed in ammoniacal tartrate solutions on warming.

Ammoniacal EDTA solutions of ferric iron (blood red) are reduced by thioacetamide and the precipitated sulfur is dissolved, but no FeS forms. Calcium may be used to counteract the EDTA and Tiron (*11*) prevents the reduction of the iron even in the presence of an excess of calcium.

Cobalt and Nickel. Neutral solutions of the divalent metals with thioacetamide remain clear and colorless even on long boiling. Ammoniacal solutions containing ammonium salts give a coarse precipitate after an incubation period and the sulfides themselves accelerate the precipitation. The precipitated sulfides show no tendency to form colloidal solutions. EDTA masks the precipitation and calcium demasks it.

Manganese. Divalent manganese behaves like nickel or cobalt. Instead of the familiar buff or pink form, a green precipitate is thrown down in high concentrations of ammonia and ammonium salts.

Selenium. Thioacetamide precipitates a yellow mixture of selenium and sulfur in hot or cold acidic solutions.

Vanadium. Thioacetamide reduces acidic solutions to vanadyl salts and no colored thiosalt can be formed by the boiling of ammoniacal solutions. On acidification, no sulfide is formed, but the solution is rendered turbid by sulfur and shows the blue vanadyl color.

Remarks

Although thioacetamide has been known for a long time, the advantages of its use in analytical chemistry have only recently been recognized and it is to be expected

that the meager facts indicated in this review will be elaborated and applied more generally.

From a practical viewpoint, thioacetamide offers so many distinct advantages over gaseous hydrogen sulfide that its use in analytical chemistry is assured.

Perhaps the chief advantage of thioacetamide, that of being a ready source of hydrogen sulfide, will guarantee its widespread use. Further, the peculiarities of its behavior, when used alone as well as in the presence of complexing agents, open many possibilities of performing separations impossible with the use of gaseous hydrogen sulfide.

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ARTICLES

Thioacetamide in the Separation and Complexometric Determination of Manganese

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The use of thioacetamide in qualitative analysis was investigated by Barber and co-workers (*1-2*) and Bloemendal and Veerkamp (*3*) since it forms metal sulfides which are coarser, less contaminated by foreign ions, and easier to filter than those obtained with hydrogen sulfide. However, when the use of thioacetamide in quantitative procedures was investigated by Flaschka and Jakobljewich (*4*), it was found that the precipitated metal sulfides were contaminated with sulfur. In spite of the fact that good results can be obtained by applying small corrections to the weight of the precipitated metals, thioacetamide precipitations are of limited value for direct gravimetric analysis. Nevertheless, thioacetamide precipitations are useful adjuncts for the preliminary separations which are commonly used in combination with titrations by ethylenediaminetetraacetic acid (EDTA) or other reagents. The literature on the analytical use of thioacetamide has been reviewed by Flaschka (*5*).

The usual method of precipitating manganese with ammonia and an oxidant such as bromine always yields precipitates which are contaminated with calcium or magnesium. The method of Ingram and Bean (*6*) is distinctly better, but it is limited to small amounts of manganese and requires a separate sample. A procedure for precipitating manganese sulfide with trithiocarbonic acid (*7*) gives good results, but the reagent is not generally available.

The following procedure involves the use of thioacetamide as a precipitant for manganese sulfide and a subsequent titration of the separated manganese with standard EDTA solution.

Reagents

Thioacetamide solution. Dissolve 2 g. of thioacetamide in 100 ml. of water.

EDTA solution. Dissolve 37.22 g. of disodium dihydrogen ethylenediaminetetraacetate dihydrate and dilute to exactly one liter with distilled water. (1 ml. = 5.493 mg. Mn.)

Buffer solution. Dissolve 13.5 g. of ammonium chloride and 88 ml. of concentrated aqueous ammonia in 250 ml. of water.

Other reagents. Ascorbic acid; 0.02 per cent methyl red in ethanol; Eriochrome Black T indicator powder (one part ground with 200 parts of sodium chloride); ammonium chloride; concentrated aqueous ammonia; dilute hydrochloric acid.

Procedure

Add not less than five times the theoretical amount of thioacetamide solution to the neutral or slightly acidic solution of manganese. Then add about 3 g. of ammonium chloride, dilute to about 100 ml. with water, and make distinctly alkaline with concentrated aqueous ammonia. Heat the solution to boiling and maintain at a near boil for about 3 minutes. Filter the hot solution through a porous porcelain crucible (A2) and wash with water.

Dissolve the precipitate in a few drops of dilute hydrochloric acid, wash the crucible well with water, and transfer the filtrate and washings to the same beaker which was used for the precipitation. Dilute the filtrate to about 50 ml. with water and boil off hydrogen sulfide. Allow to cool to room temperature, add about 3 mg. of ascorbic acid, one drop of methyl red indicator, and follow with enough aqueous ammonia until the indicator is distinctly yellow.

Add about 5 ml. of buffer solution and enough Eriochrome Black T indicator powder to give a clearly visible red color. Finally, titrate with standard EDTA solution until the indicator turns to a pure blue-green color.

Remarks

Interference by the presence of traces of heavy metals can be prevented by the addition of a few crystals of solid potassium cyanide to the ammoniacal solution before titrating.

The precipitation of manganous sulfide usually begins as soon as the solution is brought to a boil, but the precipitate may appear slowly when the amount of manganese is less than about 5 mg. Scratching the walls of the vessel often induces precipitation but small amounts of manganese, less than 2 mg., are difficult to precipitate, even on prolonged boiling with a large excess of thioacetamide. However, this is not a shortcoming of the method, because analysis for small amounts of manganese is preferably carried out by colorimetric procedures. By addition of a known amount of standard manganese solution, the concentration of manganese can be increased to about 5 mg. or more and no difficulty will be encountered in the precipitation of the sulfide. Of course, the added manganese must be subtracted from the result. An addition is also recommended when manganese in a sample must be removed prior to the determination of calcium and magnesium by EDTA.

The manganese sulfide produced by thioacetamide usually comes down in its green form, but sometimes as the buff form.

Results and Remarks

Typical results obtainable with this procedure are indicated in Table I.

Calcium or magnesium in the sample solution does not interfere since they are not contaminants of the manganese sulfide as precipitated by thioacetamide as long as carbonate-free aqueous ammonia is used. Furthermore, the calcium and magnesium content of the solution remaining after separation of manganese sulfide can be determined without error. Thus, in a mixture of Mn and Mg, the calculated amount of EDTA solution for the Mn was 5.49 ml. and 5.47 ml. were actually needed; for Mg the corresponding values were 5.24 ml. and 5.25 ml.

Inspection of the results in Table I shows that the precision and accuracy of the method depends only on the precision with which the end point of the EDTA titration can be established. In general, this will be about 1 - 2 drops of standard EDTA solution.

TABLE I
RESULTS OF MANGANESE ANALYSIS

Composition of mixture in milligrams			Mn found, in mg.
Ca	Mg	Mn	
—	—	3.9	4.0
—	—	22.6	22.6
—	—	37.5	37.2
—	—	56.7	56.7
—	75	25.4	25.3
60	—	20.6	20.4
388	60	113.5	113.5
330	30	4.6	4.7

Acknowledgment. We acknowledge our indebtedness to J. T. Baker Chemical Company for supplying us with reagent grade thioacetamide and to Messrs. Siegfried, Zofingen, Switzerland for the EDTA.

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LIGHT METAL COMPOUNDS

Tonnage Quantities for Process Use

Baker can supply these LIGHT METALS (or cations) IN THESE FORMS	Ammonium	Sodium	Potassium	Magnesium	Calcium	Strontium	Barium	Lithium
Fluoride (Bifluoride)	R (Bi)	R	R		R	PR	R	TPR
Chloride	PR	PR	PR	TPR	PR	R	PR	TPR
Bromide	PR	PR	PR		P	P		P
Bromate		PR	PR					
Iodide	R	PR	PR		R			
Sulfide	TR	PR						
Sulfite (Bisulfite)	R (Bi)	PR	P					
Sulfate	PR	PR	PR	PR	R		R	TR
Bisulfate		R	TR					
Persulfate	PR		R					
Nitrate	T PR	PR	R	TPR	TPR	PR	TPR	TPR
Phosphate	PR	R	PR	P	R			
Carbonate	R	R	R	TPR	R	R	R	TPR
Bicarbonate	R	R	PR					
Thiocyanate	TPR	PR	TPR		P			
Acetate	PR	PR	PR	R	PR		PR	
Oxalate (Binoxalate)	PR		TPR (Bi)					
Borate	P	R	P					
Dichromate	PR		PR					
Molybdate	PR	TR						
Hydroxide	PR	PR	PR	P	PR	P	R	T
Miscellaneous		CYANIDE R	FERRICYANIDE PR	[illegible]				
		SALICYLATE PR	FERROCYANIDE PR	[illegible] PR				
		BISMUTHATE R	CHROMATE PR	SILICATE P				
		STANNATE R						
		TUNGSTATE R						

KEY TO CHART

T—Technical Quality
P—Purified, U.S.P., or N.F Quality
R—Reagent Quality

Black —Carloads
Gray —Tonnage

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EDTA Titration of Palladium and Gold in Presence of Platinum

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Outokumpu Oy, Metalworks, Pori, Finland

Flaschka has described a method for the determination of silver and palladium in pure solution by means of an ethylenediaminetetraacetate (EDTA) titration of the nickel displaced from potassium nickel tetracyanide, $K_2Ni(CN)_4$, by these metals (*1, 2*). Amin (*4*) has described an EDTA procedure for silver in coinage employing Flaschka's procedure.

Experiments have shown that gold and platinum also displace nickel from $K_2Ni(CN)_4$, but that none of the other metals of the platinum group will do so (*i.e.*, iridium, rhodium, osmium, and ruthenium).

Further investigations have indicated that only approximate values for gold and palladium could be obtained when murexide was used as the indicator as in the procedure of Flaschka (*1, 2*). More satisfactory values could be obtained by determining the end point photoelectrically (*3*), but it was found that this cumbersome procedure could be eliminated by using Eriochrome Black T as an indicator and back-titrating the EDTA with a manganous sulfate solution.

On the basis of these findings Procedures *A* and *B* were developed. Procedure *A* is applicable to the determination of palladium in palladium-bearing solutions or platinum-palladium double salts. Procedure *B* is applicable to the analysis of gold in its alloys and in platinum metal.

Although Pyrocatechol Violet was found to give a good end point in the titration of nickel or palladium with EDTA, it fails in alkaline solution in the presence of platinum bcause of the formation of a complex.

Further experiments employing photometric techniques revealed that palladium forms a complex with EDTA in acidic solutions. MacNevin and Kriege (*5*) have made a similar observation and have described a spectrophotometric determination of palladium based on the formation of this EDTA complex. On the basis of these experiments and findings, Procedure *C* was developed which permits the direct titration of palladium even in the presence of platinum. Procedure *C* avoids the use of potassium nickel cyanide and employs Pyrocatechol Violet as the indicator. Procedure *C* is simpler than Procedures *A* and *B*; however, the latter procedures are preferred because of their higher accuracy.

Reagents

EDTA solution, 0.01 N. Dissolve 3.721 g. of disodium ethylenediaminetetraacetate dihydrate in one liter of distilled water. (1 ml. = 1.062 mg. Pd = 1.972 mg. Au.)

Buffer solution. Dissolve 350 ml. of concentrated aqueous ammonia and 54 g. of ammonium chloride in water and dilute to one liter.

Potassium nickel cyanide solution. A 2.5 per cent aqueous solution of the salt prepared as indicated by Flaschka (*1, 2*) or Amin (*4*).

Eriochrome Black T solution. Dissolve 1 g. of the indicator in 25 ml. of alcohol.

Manganous sulfate solution, 0.01 M. Prepare an approximately 0.01 molar solution and obtain its titre with 0.01 *N* EDTA solution.

Other reagents. Bromcresol green indicator solution; normal sodium hydroxide; 0.1 *N* hydrochloric acid; ascorbic acid; ether; nitric acid (1:1); 0.1 per cent Pyrocatechol Violet solution; 0.01 *M* bismuth nitrate solution.

Procedure A

Dissolve 1 g. of platinic ammonium chloride in water, dilute to 200 ml. in a volumetric flask, mix well, and pipette 50 ml. into a beaker.

To neutralize free acid, add 2 drops of bromcresol green indicator solution and then normal sodium hydroxide solution until the indicator turns blue. Then add 5 ml. of 0.1 *N* hydrochloric acid and pipette 10 ml. of potassium nickel cyanide solution (enough for 30 mg. of palladium). Mix well and add 5 - 10 ml. of buffer solution.

TABLE I. RESULTS OF GOLD & PALLADIUM ANALYSES

Sample and analysis	Present	Found
Pd in platinic ammonium chloride; Sample A	14.98 %	14.86; 14.99; 15.10 %
Sample B	20.85 %	20.68; 20.58 %
Au in Pt-Au solution	40.02 mg.	40.4; 40.7; 40.3 mg.
Au in Au alloy	78.36 %	78.58 %

Run in an estimated excess of 0.01 *N* EDTA solution; if the solution does not remain clear, add more buffer. After 15 minutes, add 0.1 g. of ascorbic acid, a few drops of Eriochrome Black T indicator solution and titrate the excess EDTA with 0.01 *M* manganous sulfate solution until the indicator turns red. Adjust the color of the indicator to blue with 0.01 *M* EDTA solution.

If gold is present in the sample, it will be titrated along with palladium.

Procedure B

Dissolve 0.5 g. of alloy in *aqua regia,* dilute with water and filter off any silver chloride. Dilute the filtrate to 100 ml. in a volumetric flask and mix. Pipette 20 ml. of the solution into a 100-ml. separatory funnel and add 2 ml. of concentrated hydrochloric acid.

Extract 3 to 4 times with 15-ml. portions of ether and save the ether layers. Combine the ether portions in a 400-ml. beaker, add 2 ml. each of concentrated hydrochloric and nitric acids. 10 ml. of water, and evaporate the ether on a steam bath. Continue as in Procedure *A*, starting with the line "To neutralize free acid . . ."

Procedure C

Add to a chlorine-free acidic solution of the sample, 0.01 *N* EDTA solution in excess. Dilute to 100 ml., add five drops of a 0.1 per cent Pyrocatechol Violet solution and then dilute aqueous ammonia until the indicator turns violet. Add nitric acid (1:1) until the indicator becomes yellow and then two drops in excess. Titrate with 0.01 *M* bismuth nitrate solution until the indicator becomes red-violet. Then back-titrate with 0.01 *N* EDTA solution to a yellow indicator color.

Results

Typical results for palladium and gold analyses carried out by Procedures *A* and *B* are given in Table I. The great advantage presented by these procedures is that both gold and palladium can be determined accurately without cupellation.

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An Unusual Instrument Error in Photometric Analysis

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Various errors which might be found in photoelectric filter photometers have been outlined with attention to desirable electrical and optical characteristics as well as to mechanical stability and thermal stability as they affect photocells (*1*). It is the purpose of this article to record an unusual source of instrument error which might be unsuspected in photometric studies with instruments of a particular design.

A peculiar phenomenon was encountered when a widely-used photoelectric colorimeter of U. S. design was adapted for use in studies involving rather low levels of

light striking the photocells of its voltage-balancing circuit. Plots on linear coordinate paper of transmittancy *vs.* concentrations gave curves with downward concavities between 30 and 70 per cent transmittancy values.

The cause of this unexpected behavior was traced to the pilot light used to illuminate the galvanometer and the slidewire scale of the instrument. With the primary exciter lamp off and with both photocells disconnected, the galvanometer pointer moved from a zero position to give a small displacement to the right, and then moved back again to zero as the slidewire contact was moved from the 10 per cent to the 100 per cent transmittancy position.

The maximum galvanometer displacement corresponded to about the 55 per cent transmittancy position. The pilot light is mounted about 1.5 inches above this position and is a 3-watt, 110-volt bulb of the candelabra type. Thus, the lamp creates thermal potentials in the slidewire. In effect, the midposition becomes the hot junction of a thermocouple with the ends of the slidewire acting as cold junctions. Figure 1 shows the magnitude of this thermal potential which opposes the normal potential developed by the photocells.

Measurement of Error

Measurements were made to determine the effect of this error when using the colorimeter under normal operating conditions, that is, at other than low light levels. First the pilot light was turned off, the slider was set approximately at the 55 per cent transmittancy position, and the galvanometer was brought to zero by adjusting the ungraduated resistor shunted across the working photocell. Next, with a recommended light intensity striking the photocells, the potential developed between the 10 per cent and the 55 per cent transmittancy positions on the slidewire was measured with a potentiometer. This potential is of the order of 5-8 millivolts and depends upon the particular instrument tested and the absorbance of the color filter used. Thus, the error in the slidewire potential values at the midpoint of the per cent transmittancy scale will range from 1-2 per cent, or even greater at low levels of illumination where the photocell output is low and the error contributed by the thermal potential is relatively greater.

Attempted Reduction of Error

Attempts have been made to reduce the thermal potential by coating the pilot light with aluminum paint over the portion of its surface which faces the slidewire, by suspending a strip of aluminum metal or foil between the bulb and slidewire, and by wrapping paper-backed aluminum foil around the circular Bakelite housing of the slidewire. Any one of these expedients reduced the thermal potential to about 0.02 millivolt; a combination of any two dropped the potential to about 0.01 millivolt. Aside from turning the lamp off, it did not seem that greater reduction could be accomplished easily.

Remarks

The authors admit that these instruments are not designed for work involving low levels of illumination. In many routine

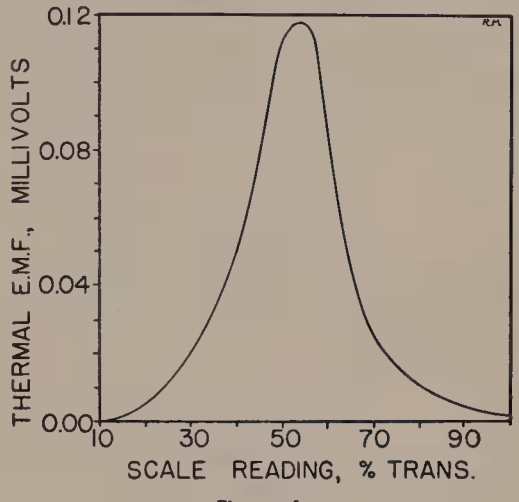

Figure 1.

colorimetric studies, the accuracy may be sufficiently great since the use of a calibration curve will compensate partially for the thermal potential error. However, to gain maximum accuracy and precision from this and similar instruments, it seems almost inexcusable to add this source of error to the many other mechanical systematic, and operational errors (2) encountered in photometric analysis. Instrument manufacturers should assume full responsibility for the elimination of this error in future models.

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Colorimetric Determination of Borate with Polyvinyl Alcohol-Borate-Iodine Complex *

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Polyvinyl alcohol-borate esters react with iodine in acid solutions to give a blue color which can serve for the rapid identification of borates (*1 - 2*). The blue color is presumably a colloidal addition compound of iodine and polyvinyl alcohol borate ester, because a blue precipitate can be isolated from concentrated solutions of the reactants. Apparently the composition of the complex is variable and may be affected by the conditions under

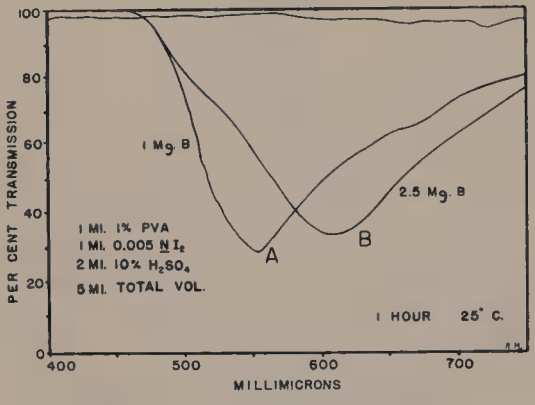

Fig. 1. Spectral Transmission of PVA-Borate-Iodine Complex.

which it is formed as well as by the nature of the polyvinyl alcohol (PVA). Although West (*1*) found that the addition compound he isolated had a maximum absorption at 670 millimicrons, in the experiments reported here PVA samples of different molecular weights consistently yielded addition compounds with an absorption maximum of about 565 millimicrons in dilute colloidal suspension. In more concentrated suspensions and in dry films the maximum is shifted to only slightly higher wavelengths (Figure 1).

* Partial summary of a thesis for the M. S. degree presented to the faculty of Lehigh University by E. S. Jacobs.

Nature of Color System

Preliminary experiments with Wirth's procedure (*2*) showed that the formation of the blue color is critically dependent upon the relative amounts of the reactants, that its intensity can not be reduced proportionally by dilution, and that under certain conditions a blue color can be developed even when borates are absent. As was observed by Wirth (*2*), red to green colors form immediately with a certain order of addition of reagents; however, it has been found that any order of addition will give a blue color after a half hour in the procedures described below.

The variables affecting the color reaction were systematically studied and the results are summarized in Figure 2. This figure is a three-dimensional representation of the four major parameters controlling the color formation: the concentrations of PVA, acid, iodine, and borate. The other parameters, time, temperature, and total concentration were maintained constant.

Referring to Figure 2, any mixture of solutions of 10 per cent sulfuric acid, 1 per cent PVA solution, and 0.005 *N* iodine solution totaling 100 ml. and occurring within the surfaces of the solid will give a blue color only when the indicated amount of borate is present. Mixtures corresponding to points to the right, between the solid and the plane *BCDE,* will produce a blue color even when borates are absent, while mixtures between the solid and the plane *ACDF* will not form a blue color under any circumstances. Furthermore, as the amount of borate is diminished, the ratio of PVA, acid, and iodine becomes more critical; at a value corresponding to about 7 milligrams of boron per 100 ml., the ratio is unequivocally defined. There exists no other mix-

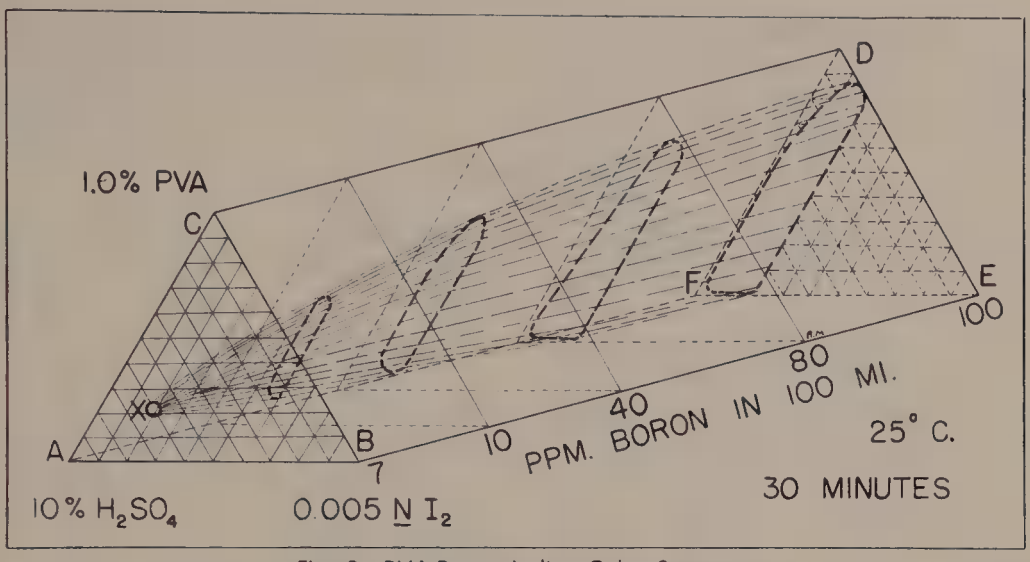

Fig. 2. PVA-Borate-Iodine Color System.

ture of PVA, acid, and iodine which will produce a distinguishable blue color within 30 minutes with smaller amounts of borate.

Detailed studies of the effects of variations in time, temperature, and concentration of each reagent did not lead to a significant increase of the sensitivity of the reaction as a test for borates. On the other hand, some substances were found which tend to inhibit the formation of the blue color (*e.g.*, thiocyanates), and others to reduce the time required for its formation, notably ferric ion. Although the ions which accelerate the color formation are useful adjuncts for a qualitative procedure, unfortunately they tend to equalize the intensity of the color produced by different amounts of borate and can not be used to advantage in quantitative procedures.

Basis of Analytical Procedures

The following procedures were developed on the basis of the studies of the color system outlined above and are predicated on the use of the concentrations of PVA, iodine, and acid corresponding to point *X* in Figure 2.

Reagents

PVA solution, 1%. Prepare a one per cent solution by sprinkling 10 grams of polyvinyl alcohol (Du Pont "Elvanol" No. 70-05) into one liter of cold water, while stirring vigorously. After a slurry is obtained, heat to at least 75° C. and continue stirring until the solution is clear and colorless. Other grades of PVA may be used, but the completely hydrolyzed, low viscosity polymers give the best results and are easier to handle.

Sulfuric acid, 15%. Mix 150 ml. of concentrated sulfuric acid with 850 ml. of water.

Iodine solution, 0.02 N. Dissolve 1.27 grams of iodine and 3 grams of potassium iodide in a small amount of water and dilute to 100 ml. Take 50 ml. of this 0.1 *N* solution and dilute to 250 ml. to make a 0.02 *N* solution of iodine.

Standard borate solution. Dissolve 88.14 grams of reagent grade $Na_2B_4O_7.10H_2O$ in 750 ml. of water, neutralize with sulfuric acid and dilute to a total volume of 1000 ml. Take 100.0 ml. of this stock solution and dilute to one liter with water. (1 ml. = 1.0 mg. B = 3.23 mg. B_2O_3.)

Ferric sulfate solution. Dissolve 10 grams of reagent grade ferric sulfate (assay about 73 per cent) in 75 ml. of water. Heat to 60° C. and add 2 ml. of concentrated sulfuric acid. The solution should be clear; if not, add more acid. Dilute to 100 ml. with water.

Qualitative Procedure

Mix one ml. of PVA solution with not more than 3 ml. of a neutral solution containing borate. Add 1.30 ml. of 15 per cent sulfuric acid solution and mix. Add 0.10 ml. of ferric sulfate solution, dilute to about 5 ml. with water and add one drop of 0.1 *N* iodine solution. Mix well. Prepare a blank using 3 ml. of water and allow both the blank and the sample to stand for thirty minutes. A blue color in the sample indicates borate. The blank should be colored yellow.

Quantitative Procedure

In a 10-ml. volumetric flask, put 2 ml. of PVA solution and add 2.5 ml. of a neutral solution containing 0.75 to 2.0 mg. of boron. Mix and add 4.0 ml. of 15 per cent sulfuric acid solution. Dilute to about 8 ml. after mixing well and then add 0.50 ml. of 0.02 *N* iodine solution. Bring to the mark, mix well, and allow the color to develop for one hour. Prepare a blank using water in place of the sample.

Determine the per cent transmission of the sample against the blank at 565 millimicrons with a spectrophotometer or a colorimeter using a green filter. The amount of borate present in the sample is determined from a calibration curve prepared by using 0.00, 0.80, 1.00, 1.25, 1.50, and 2.00 ml. of the standard borate solution. A calibration curve must be carefully established since the plot of optical density *vs.* concentration of borate is not linear, especially at low concentrations (see Figure 3). If a sample gives a blue

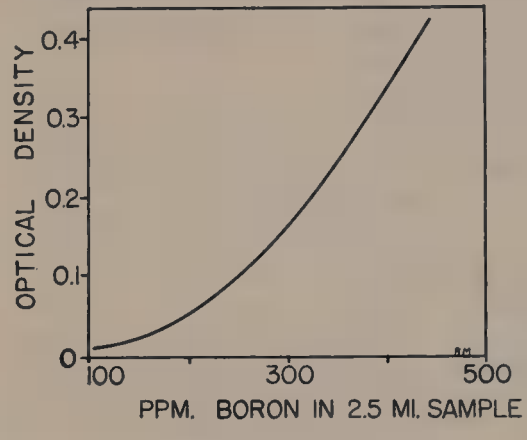

Fig. 3. Calibration Curve.

color of optical density greater than 0.4, repeat the determination using a smaller aliquot because the intensity of the blue color can not be reduced proportionally by dilution.

Remarks

Table I lists the maximum allowable amounts of a number of ions which may be present in the sample used in both procedures. As can be seen, the qualitative procedure can be applied to almost any kind of sample, particularly if reducing substances are absent.

Most of the ions which seriously interfere with the procedures can be removed by oxidation or sulfide precipitation.

TABLE I
INTERFERENCES IN BORON PROCEDURES

Ion	Max. ppm. of ion permissible in sample Qual.	Quant.
Ag^{+}; Ba^{+2}; Ca^{+2}; Sr^{+2}; Pb^{+2}; Hg_2^{+2}	pptn.	pptn.
AsO_2^{-}; Sn^{+2}	0	0
Ti^{+3}; Cr^{+3}; $Fe(CN)_6^{-4}$; $Fe(CN)_6^{-3}$	500	100*
CNS^{-}	500	100†
Co^{+2}; Cu^{+2}; Fe^{+3}; Mn^{+2}; Ti^{+4}	1,200	200
Cd^{+2}; Ni^{+2}; Zn^{+2}; MoO_4^{-2}	3,000	400
Al^{+3}; Hg^{+2}; Sb^{+3}	8,500	1,000
AsO_4^{-3}; NH_4^{+}; Sn^{+4}; oxalate; acetate; tartrate; citrate	15,000	2,000
PO_4^{-3}; SO_4^{-2}; Cl^{-}; Na^{+}; K^{+}	No interference	

* Color of the ions interferes.
† Inhibits color formation.

Those ions which precipitate as sulfates or iodides are centrifuged off after insuring their complete precipitation by adding an excess of iodide prior to the addition of 0.02 *N* iodine solution. For extreme cases, cation exchange resins for the removal of interferences have already been suggested (*3*), and in any event, the preliminary distillation of borate as trimethyl borate is applicable.

In the qualitative procedure, the blue color forms immediately when the borate concentration in the 3-ml. sample is greater than about 300 ppm. of boron, but 80 ppm. can be easily detected on standing 30 minutes. If the concentration of ferric ion in the sample solution is greater than about 1200 ppm., a blue color will form even in the absence of borates.

Investigation has also shown that large amounts of organic materials such as acetone, *N,N'*-dimethylformamide, dioxane, ethanol, methanol, formic acid, and pyridine destroy the blue color, while chloroform, cyclohexane, 1,1-dichloroethane, ether, and iso-amyl acetate extract iodine from the addition compound and cause the color to fade. Glycerine, phenol, and sucrose do not interfere.

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Microvolumetric Determination of Silver and Copper in Coinage

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The usual methods for the determination of silver and copper in metallurgical products are time-consuming and critically dependent upon conditions which are sometimes difficult to achieve. Volumetric procedures employing ethylenediaminetetraacetic acid (EDTA) have found wide application but are based on the use of precipitants or other complexing agents since EDTA is relatively non-specific or selective in its reactions. For example, Flaschka (1) determined copper directly with EDTA using murexide as indicator after separation of interfering metals by various precipitants.

It has been found that the analysis of silver-copper alloys by EDTA titration is possible without preliminary separations or the addition of complex masking agents because copper forms the more stable complex. In the following procedure, copper is titrated in a slightly ammoniacal solution with EDTA using murexide as indicator; silver is then permitted to react with potassium nickel tetracyanide, whereby a corresponding amount of nickel is liberated:

$$2\,Ag^{+} + [Ni(CN)_4]^{-2} = 2[Ag(CN)_2]^{-} + Ni^{+2}$$

The liberated nickel ions are then titrated with EDTA in the presence of murexide as indicator (2).

Reagents

EDTA solution. Dissolve 3.722 g. of disodium ethylenediaminetetraacetate dihydrate in water and dilute to one liter. (1 ml. = 653.7 micrograms of Cu or 2157.6 micrograms of Ag.)

Buffer solution. Dissolve 13.5 g .of ammonium chloride in water, add 88 ml. of concentrated aqueous ammonia, and dilute to 250 ml.

Potassium nickel tetracyanide (3). Dissolve 25 g. of nickel sulfate heptahydrate in 50 ml. of distilled water and slowly add 25 g. of powdered potassium cyanide with frequent agitation. A syrupy liquid and a white deposit of potassium sulfate forms. Gradually add to the liquid 100 ml. of 95 per cent ethanol and stir well. Filter off the deposited potassium sulfate with the aid of suction and wash twice with 2-ml. portions of ethanol.

Evaporate the filtrate at about 70° C. (An infrared lamp is ideal for this purpose). Stir to facilitate formation of a crystal slurry; just before the slurry becomes stiff (nearly dry), remove the source of heat and let the mass cool. Mix the crystals with 50 ml. of alcohol, filter by suction, and wash twice with 2-ml. portions of alcohol.

Spread out the fine yellow needles into layers and allow to dry for several days at room temperature. During this period, excess potassium cyanide will be converted to carbonate.

Test the preparation by dissolving 100 mg. of the salt in 10 ml. of water, adding 0.5 ml. of concentrated aqueous ammonia, and a small amount of murexide indicator powder. The solution should be wine-red in color and the addition of a drop of 0.01 molar nickel or silver solution should change the color to yellow; the addition of EDTA should cause the indicator color to change to a deep blue or violet.

Additional reagents. Murexide indicator powder (1 part of the indicator ground with 400 parts of sodium chloride); nitric acid.

Procedure

Dissolve 4-5 mg. of the sample in 1 ml. of concentrated nitric acid and 5 ml. of water. Evaporate nearly to dryness, dissolve the residue in about 10 ml. of water, transfer to a 25-ml. volumetric flask, and bring to the mark with water.

Pipette 5 ml. of this solution into a 50-ml. Erlenmeyer flask and add buffer solution dropwise until the precipitate which first forms redissolves and the solution is distinctly ammoniacal. Avoid a large excess of the buffer.

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Dilute with water until the solution is 0.01 to 0.1 molar in ammonia. Generally, about 0.25 ml. of buffer will be required. Then add 0.2 - 0.4 mg. of the indicator powder. The resulting solution should be colored yellow; if not, too much ammonia is present and it will be necessary to dilute the solution until the yellow color appears.

Titrate the yellow solution with standard EDTA solution very slowly until the color becomes permanently purple-red. Record the volume of EDTA required; this is equivalent to the copper in the sample.

Add about 4 mg. of solid potassium nickel tetracyanide to the solution remaining after the titration of copper and stir well. The indicator will turn back to the original yellow color. Now titrate the liberated nickel ions with standard EDTA solution until the color of the indicator becomes purple-red. This volume of EDTA is equivalent to the silver present in the sample.

Results and Remarks

Table I shows the accuracy and precision which can be obtained with the above procedure using synthetic mixtures of copper and silver solutions. The maximum error in the micro-titration of copper is about 0.004 ml. in a volume of 1.544 ml., and the error in the titration of silver is about 0.003 ml. These errors are small enough to be ignored in such analyses.

TABLE I. TYPICAL RESULTS OBTAINED FOR ANALYSIS OF SILVER AND COPPER

Sample	Copper, μg. present	Copper, μg. found	Silver, μg. present	Silver, μg. found
A	100	98	165	166
B	100	99	330	328
C	100	100	494	491
D	300	303	659	663
E	400	398	330	328
F	400	399	1648	1657
G	1000	994	165	163

Only thirty minutes are required to carry out the procedure, including weighing of the sample and calculation of the results.

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Determination of Tartrate in Copper Cyanide Baths

OTTO ALCIDES OHLWEILER and JORGE OLIVEIRA MEDITSCH

Escola de Engenharia, P. Alegre, Brazil

Tartrate in copper cyanide baths is usually determined by oxidation with permanganate after free cyanide is removed by precipitation with silver nitrate (*1, 2*). In the usual procedures, the sample solution is neutralized to phenolphthalein and then treated with silver nitrate in the presence of nitrobenzene to coagulate the precipitate. When sufficient silver has been added, the white precipitate of silver argentocyanide changes to blue-gray. However, this color change does not always take place in the presence of nitrobenzene, and it was found that an end point could be observed without it, both by coagulation of the silver cyanide and by a change in color. The following procedure has been found to yield consistently satisfactory results in spite of the fact that the silver argentocyanide must be removed by filtration.

Reagents

Standard solutions, 0.1 N. Prepare and standardize in the usual fashion 0.1 *N* solutions of potassium permanganate and sodium thiosulfate.

Other reagents. Phenolphthalein powder or indicator solution; one per cent sulfuric acid; twenty per cent sulfuric acid; ten per cent silver nitrate solution; manganous sulfate; potassium iodide; one per cent starch solution.

Procedure

Pipette a 5-ml. sample into a 250-ml. volumetric flask, add 100 ml. of water, some phenolphthalein, and then add one per cent sulfuric acid, dropwise, until the pink color disappears. Now add drops of 10 per cent silver nitrate solution until the precipitate changes from white to gray. Continue agitating

for a minute longer and test for complete precipitation by adding another drop of silver nitrate solution. Bring to the mark and filter through fine-grain retentive paper.

Pipette 50 ml. of the filtrate into a 500-ml. Erlenmeyer flask, add 5 ml. of 20 per cent sulfuric acid, 5 grams of manganous sulfate, and 100 ml. of water. Heat to about 70° C. and then slowly add, with agitation, exactly 20 ml. of standard 0.1 *N* permanganate solution. Allow the hot solution to stand for 5 minutes and then cool to room temperature under running water.

Add 2 grams of potassium iodide and 2 ml. of one per cent starch solution. Mix well and then titrate with 0.1 *N* sodium thiosulfate solution until the blue color disappears for at least one minute.

Calculation

The grams per liter of Rochelle salt in the bath is given by the expression: $47[20(\text{norm. } KMnO_4) - (\text{ml. x norm. } Na_2S_2O_3)]$.

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Estimation of Arsenic by Paper Chromatography

I. I. M. ELBEIH

Chemistry Department, University of Cairo, Giza, Egypt

An earlier communication (*1*) suggested that trivalent arsenic can be separated chromatographically from common metals by using a saturated butanol-water solution containing ammonium tartrate, ammonium borate, and mannitol. Furthermore, a special test for arsenic was reported which consisted of spraying the chromatogram with alcohol containing one per cent nitric acid and five per cent glycerol and, after drying, of spraying with ammoniacal silver nitrate solution. Presumably, the arsenic spot is converted to yellow silver arsenite which, on irradiation with ultraviolet light while still wet, is changed to brown silver arsenate and black metallic arsenic. The spot is easily visible against the purplish background of reduced silver nitrate. By this method, it is possible to detect the presence of 0.3 micrograms of arsenic in 0.01 ml. of sample solution.

Further experiments have shown that this procedure is applicable only if the sample is neutral, alkaline, or weakly acid. Although excess acidity does not affect the separation of arsenic from other cations on the sheet chromatograms, it was found that when acidic solutions are used, a black color envelops the arsenic spot and prevents identification.

Apparatus

The apparatus is similar to that already in general use for paper chromatography (*2-4*) and consists of a glass trough supported in a glass tank 50 x 25 x 15 cm. tightly covered with a glass plate. In the trough is put the alcoholic layer of the solvent and at the bottom of the tank is placed a Petri dish containing the aqueous layer of the solvent. The tank is kept at a constant temperature. Filter paper sheets (Whatman No. 1) are cut into strips 20 cm. wide and 40 cm. long and the trough height is adjusted to permit hanging two of these strips, one from each side of the trough, with their top edges dipping into the solvent.

Reagents

Butanol-water solvent. Dissolve 1 g. of ammonium borate, 1 g. of ammonium tartrate, and 0.5 g. of mannitol in 50 ml. of water. Place this solution in a separatory funnel and mix thoroughly with 50 ml. of *n*-butanol. Let the mixture stand until both layers become clear. Drain the aqueous layer into the Petri dish of the chromatographic tank and put some of the alcoholic layer in the trough.

Nitric acid-glycerol solution. Prepare an alcoholic solution 1 per cent in nitric acid and 5 per cent in glycerol.

Ammoniacal silver nitrate solution. Add concentrated aqueous ammonia to a well-agitated solution of 5 g. of silver nitrate in 100 ml. of water until the precipitate which initially forms is completely dissolved.

Standard Arsenic Solutions. Prepare a series of solutions of sodium arsenite containing 0.1,

0.05, 0.01, 0.005, 0.004, and 0.003 per cent arsenic. These solutions should be made nearly neutral.

Procedure

The solution to be analyzed for trivalent arsenic must be highly concentrated by evaporating a large known volume under reduced pressure and at about 40° C. to avoid volatilization of arsenic. The sample solution should be nearly neutral or very slightly alkaline before concentration. For convenience, a graduated tube may be sealed to the bottom of the distilling flask so that volumes of sample as large as 100 ml. can be evaporated to a known volume of 10 ml. or less.

Take drops (0.01 ml.) of the nearly neutral sample solution and drops of the standard arsenic solutions and place them individually at distances of about 4 cm. apart on a pencilled line 8 cm. from the top edge of the filter paper sheets. Then, put the top edge of the paper in the trough and close the tank. Let the strips stand until the liquid front is about 5 cm. from the lower edge of the paper.

Dry the chromatograms in a stream of hot air; spray with nitric acid-glycerol solution and once again dry the strips in a stream of hot air. Finally, spray with ammoniacal silver nitrate solution and, while wet, irradiate with ultraviolet light.

Compare the intensity of the color of the spot formed by the sample solution with the colors formed by the standard arsenic solutions. Estimate the concentration of arsenic in the sample, taking into account the concentration factor introduced by evaporation of a large volume of original sample solution.

Results and Remarks

Typical results obtained with this procedure are indicated in Table I; the highest R_f value observed for the cations in the six samples was in the range of 0.18 to 0.20. Only trivalent arsenic responds to this procedure since pentavalent arsenic shows an R_f value of zero. Antimony, tin, and mercury do not interfere and it is possible to detect 0.3 microgram of arsenic in 0.01 ml. of sample solution by this procedure.

TABLE I. TRACE TRIVALENT ARSENIC ANALYSIS IN MIXED SALTS

Per cent cations in sample*	Per cent As^{+3}† taken	found
A: Cu^{+2}, 1.3; Cd^{+2}, 1.8; Sb^{+3}, 2.0; Hg^{+}, 3.6; K^{+}, 31.0	0.015	0.015
B: Hg^{+2}, 3.0; Fe^{+3}, 0.3; Co^{+2}, 0.6; Ca^{+2}, 3.3; Na^{+}, 20.3	0.023	0.022
C: Cu^{+2}, 2.6; Cd^{+2}, 3.6; Fe^{+3}, 1.4; Sn^{+2}, 5.3; Zn^{+2}, 13.2	0.015	0.015
D: K^{+}, 25.0; Ca^{+2}, 4.4; Pb^{+2}, 3.1; Mn^{+2}, 1.1; Ni^{+2}, 1.0	0.0076	0.007
E: Cu^{+2}, 1.9; Hg^{+2}, 2.9; Na^{+}, 19.0; Sn^{+2}, 1.0; Mg^{+2}, 1.4	0.009	0.008
F: Cu^{+2}, 2.6; Cd^{+2}, 3.6; K^{+}, 39; Zn^{+2}, 2.2; Sr^{+2}, 4.2	0.018	0.017

* Cations added as nitrate except Sb^{+3} as $Sb_2(C_4H_4O_6)$, Sn^{+2} as $SnCl_2$, Sn^{+4} as $SnCl_4$.
† As^{+3} added as As_2O_3 in samples A - D, and as Na_2HAsO_3 in E and F.

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Ferrate Oxidation of Iodate to Periodate

JAMES M. SCHREYER*

University of Kentucky, Lexington, Kentucky

Periodates are usually prepared by the oxidation of iodates with chlorine in strongly alkaline solution. Oxidations in strongly alkaline solution with the ferrate (VI) ion have been reported (*1* - *3*), and it is the purpose of this paper to indicate that this ion can also oxidize iodate.

The formation of periodate was confirmed by conversion of manganous ion to per-

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manganate followed by titration with standard ferrous sulfate (after removal of iodate).

Reagents

Alkaline iodate solution. Prepared by dissolving 8 g. of sodium iodate in 300 ml. of hot water and adding 300 ml. of saturated sodium hydroxide solution.

Potassium ferrate (VI). Prepared by the method of Thompson, *et al.* (4).

Phosphoric Acid Solution. A mixture of 150 ml. of syrupy phosphoric acid, 60 ml. of concentrated sulfuric acid, and 240 ml. of water.

Experimental

A weighed sample of about 0.1 g. of potassium ferrate (VI) was added to 25 ml. of alkaline iodate solution. Immediate oxidation of the iodate ion to periodate was evidenced by the complete disappearance of the red ferrate color and the precipitation of white sodium paraperiodate, $Na_3H_2IO_6$. This solution was acidified with 20 ml. of phosphoric acid solution, 70 ml. of 2:1 sulfuric acid were added, brought to a boil, and then 20 ml. of saturated manganous sulfate solution were added. The purple permanganate color developed immediately. The hot solution was treated with 2 g. of mercuric nitrate, cooled, and filtered through fine sintered glass into 50 ml. of standard ferrous sulfate solution. The excess ferrous salt was back-titrated with standard permanganate.

Results and Remarks

The oxidation of iodate to periodate by ferrate (VI) is described by the following:

$$2\ FeO_4^{-2} + 3\ IO_3^- + 9\ Na^+ + 2\ OH^- + 11\ H_2O = 2\ Fe(OH)_3(H_2O)_3 + 3\ Na_3H_2IO_6$$

In a series of experiments, potassium ferrate (VI), which analyzed 91.85 ± 0.13 per cent K_2FeO_4 by the chromate method (3), oxidized iodate to periodate with an efficiency of 98 per cent.

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Borate—Fluoride Samples for Qualitative Analysis

FRANKLIN B. WELLS

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Powdered samples for qualitative analysis containing certain proportions of calcium fluoride and borax gave negative tests for fluorides after prolonged storage. In all instances, boron could be detected by the usual flame tests in samples moistened with acid. However, tests for fluoride by etching of glass were generally unsuccessful on aged samples.

The influence of aging and the ratio of components on the fluoride test are summarized in Table I. Apparently, the rate of formation of fluoborate ion is slow enough to permit detection of fluoride in a freshly prepared sample containing at least 20 per cent calcium fluoride.

As the samples age, fluoborate forms and the probability of detecting fluoride diminishes. However, if the sample contains more calcium fluoride than is required to complex the borate (theoretical ratio: 62 CaF_2 to 38 borax), the fluoride test will be positive, regardless of the age of the sample.

TABLE I. RESULTS OF FLUORIDE TEST

Days Stored	Ratio of fluorite to borax 20:80	40:60	60:40	80:20
0	M	S	S	S
7	N	W	S	S
14	N	N	W	S
42	N	N	N	S
21	N	N	N	S

M = Moderate; S = Strong; W = Weak; N = Negative

Determination of Silver in Refined Bismuth

WALTER D. NORDLING

Grinnell Corporation, Providence, Rhode Island

The precipitation of silver with 1,2,3-benzotriazole (*1*) has been shown to be nearly specific from ammoniacal solutions of ethylenediaminetetraacetic acid (EDTA), but there has been no study reported of the precipitation in the presence of bismuth. Experiments have shown that bismuth does not interfere and that it is possible to determine from 0.10 to 0.01 per cent silver in refined bismuth by the following procedure.

Reagents

1,2,3-benzotriazole solution. Dissolve 2.50 g. in 30 ml. of concentrated aqueous ammonia and dilute to 100 ml. with water.

Other reagents. Nitric acid (3:7); disodium salt of EDTA dihydrate; concentrated aqueous ammonia.

Procedure

Dissolve 15 g. of bismuth drillings in a 400-ml. beaker with 100 ml. of nitric acid (3:7). Boil the solution to expel nitric acid fumes. Add 30 g. of disodium EDTA dihydrate. If necessary, warm to complete solution. Cool, add about 30 ml. of concentrated aqueous ammonia and then filter. Dilute the filtrate to 300 ml. Assure that the solution is slightly alkaline and then add 10 ml. of benzotriazole solution. Digest at 80° C. for 30 minutes.

Filter the hot solution through a medium porosity sintered-glass crucible, wash the precipitate five or six times with 10-ml. portions of hot water, and dry at 100° C. for 1 to 2 hours. The weight of the precipitate multiplied by 0.4774 equals the weight of the silver in the sample.

TABLE I. TYPICAL RESULTS

Sample	Per cent silver present	Per cent silver found
A	.033	.032
B	.061	.063
C	.090	.090

Results

The values given in Table I show the accuracy obtained with this method on synthetic samples.

LITERATURE CITED

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Purification of Cyclohexane

NILS ANDREAS SÖRENSEN

Inst. for Org. Kjemi, Norges Tek. Högskole, Trondheim, Norway

The following procedure for the purification of cyclohexane for ultraviolet spectroscopy requires no special equipment and does not use fuming sulfuric acid (*1*). Furthermore, it yields a product of such purity that a final distillation is unnecessary.

Procedure

Vigorously stir the crude solvent for about 3 hours with 10 per cent of its volume of a 1:1 mixture of 98 per cent sulfuric acid and 68 per cent nitric acid. Decant the solvent layer, wash once or twice with water, and then dry over anhydrous sodium sulfate.

Filter no more than 5 liters through a 2 x 10-inch column of activated alumina. Sulfur and nitro-compounds are quantitatively absorbed by the alumina and distillation is unnecessary.

LITERATURE CITED

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Containers for Baker chemicals must meet the primary requirement of safeguarding quality. They also must be safe and convenient to use, store, and move from one point to another. Our packaging engineers are constantly working on new materials and better design for containers. These studies cover every detail—not only the construction, shape and composition of the containers themselves but also the closures, cap liners, film seals, etc.—to insure that the entire package is the best one for each chemical. This page shows just a few of many recent improvements.

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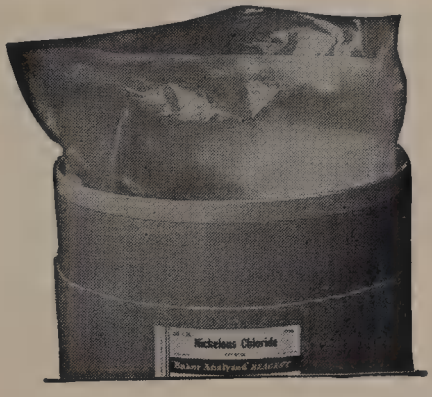

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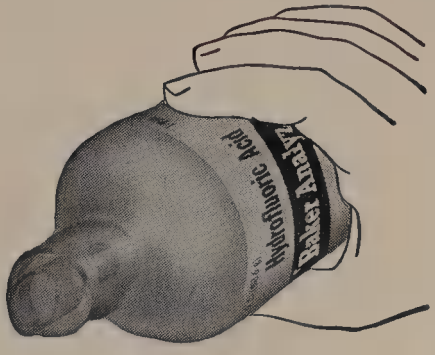

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Improvement of Koch Microburette

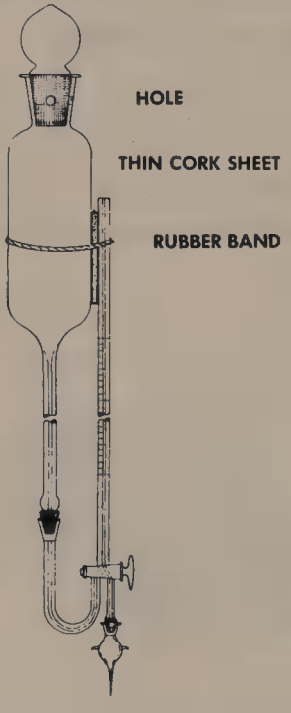
M. R. VERMA and V. M. BHUCHAR

National Physical Laboratory of India, New Delhi, India

Commercially available apparatus can be readily modified to conform with the illustrated microburette. Burettes of this design can be easily dismantled for cleaning, have parts which are readily interchangeable if broken, and are less easily broken in transit.

All connection tubes are of glass, and the burettes can be safely used with oxidizing or biological solutions which are liable to be affected by rubber connections (*1*).

The usual platinum alloy delivery tube is replaced by a finely drawn glass tip.



This permits regulation of the size of the drops delivered and permits cheap replacement of a damaged tip.

For ease of filling the burette, two holes which are in alignment are provided in the stopper and mouth-wall of the reservoir. For use with solutions containing volatile constituents, the reservoir can be closed by turning of the stopper.

Acknowledgment. We acknowledge the help of S. D. Paul in testing such burettes and the kind permission of the Director of the National Physical Laboratory to publish.

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Solubility of Silicone Stopcock Grease

DAVID TABER

Dept. of Ind. Medicine, New York University Postgraduate Medical School, New York, N. Y.

Although silicone stopcock grease finds widespread use in the laboratory because of its chemical inertness, its solubility in organic solvents is seldom recognized. Thus, when 1.95 g. of Dow-Corning silicone stopcock grease was treated with petroleum ether (b.p., 30 - 60°C.) for 7 hours in a Soxhlet apparatus, 1.72 g. (88.2 per cent) was extracted. Under the same conditions, acetone removed 0.80 g. (43.5 per cent) from 1.84 g. of grease.

The solubility of silicones in ordinary organic solvents is sufficient to limit their utility when the exclusion of artifacts is essential.

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Constant Level Device for Water Baths

ALEXANDER VAN HOOK

Holy Cross College, Worcester, Mass.

The problem of constantly refilling water baths can be conveniently solved by the use of float valves for chicken watering pans commercially available at about $2.00. The valve is mounted on 3/8-inch pipe and connected to service lines by rubber tubing or piping.

Thermostat Spark Shield for Ovens

C. JAMES CONNER
Rheem Mfg. Co., New Orleans, La.

Many laboratories have been using drying ovens with exposed thermostat contacts in atmospheres of flammable solvent vapors without considering the make-and-break spark of the contact points.

A degree of protection is afforded by covering the entire external thermostat assembly, which is usually located on the top of the oven, with an inverted 800-ml. beaker. Although the use of a beaker is effective, a wide-mouth jar or bottle is even more efficient because the mouth fits flush with the oven top.

The covering of external thermostat contacts is an important safety precaution when flammable solvents are apt to be present through spillage or other accidental means.

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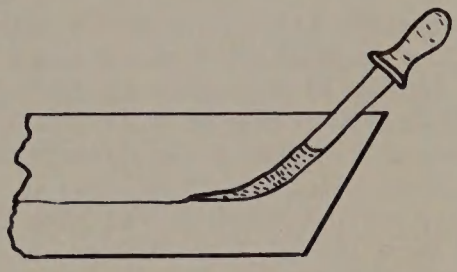
Teflon Barriers for Paper Chromatography

EARL USDIN
Institute for Cancer Research and The Lankenau Hospital Research Institute, Philadelphia, Pa.

When paper chromatograms are spotted closely, there is often doubt as to the exact origin of certain spots. This is particularly true in the case of compounds of high R_f values where there may be a large lateral movement during development. If solvent-proof barrier lines are drawn the length of the paper and samples spotted between them, each unknown will be completely confined to one narrow strip of paper.

A satisfactory material for making such solvent-proof barriers is Teflon Resin Dispersion, available from the Polychemicals Department of E. I. DuPont de Nemours and Co., Wilmington, Delaware. The easiest method of applying the dispersion is with a medicine dropper bent at 45° and having a capillary tip. As illustrated, the dispersion is streaked on the paper by drawing the dropper along it while pressing on the rubber bulb. The width of the



Teflon barrier is controlled by the rate of streaking, the pressure on the bulb, and the diameter of the capillary.

This technique may also be used in place of rather expensive and short-lived brushes for streaking reagents on columnar chromatograms.

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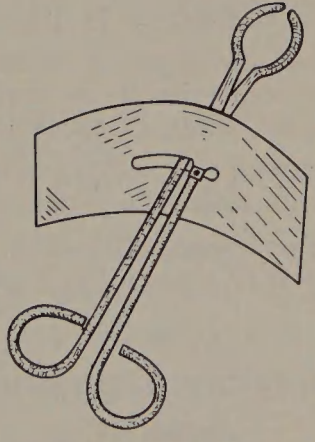
Shielded Furnace Tongs

R. F. MURACA
Lehigh University, Bethlehem, Pa.

The illustrated furnace tongs feature a shield for the protection of the hand from radiant heat when removing crucibles



from muffles. The shield consists of a piece of 0.03-inch aluminum shaped as indicated and riveted to one arm of a pair of ordinary crucible tongs.

Leaded Glass Test for Fluoride

ARCOT VISWANATHAN and **SYED AZMATULLAH**
The New College, Royapettah, Madras, India

Mannheimer (*1*) has reported a method for the detection of fluorides based on the etching of lead glass by hydrogen fluoride evolved from an acidified sample. However, lead glass is not always readily available. It has been found that it can be replaced by a rod of soda glass that has been treated with litharge in an oxidizing flame.

Preparation of Leaded Glass

Coat one end of a soda glass rod with a thin paste of litharge and water and heat in an oxidizing flame until the coating disappears as a transparent part of the glass. Reheat the rod in a reducing flame until a faint, but distinct, area of metallic lead appears on the surface.

Detection of Fluoride

Hold the rod in the vapor evolved from a sample acidified with sulfuric acid and warmed. If fluoride is present in the sample, the black color of lead disappears from the rod. The disappearance of the metal is best observed by washing the rod with water. The metallized surface can be restored by reheating the rod in a reducing flame; and, therefore, a single rod can be used repeatedly.

Remarks

For convenience, such rods may be kept in store for repeated use with the metallized ends thickened and rounded to distinguish them from the untreated ends.

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NOTES OF INTEREST

Reprints Available

A reprint of the review and article on thioacetamide in this issue with price information is available without obligation by writing J. T. Baker Chemical Co., Dept. C-T, Phillipsburg, N. J.

Reprints of the following items that appeared in recent issues are available by writing The Editor, CHEMIST-ANALYST:

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'Laboratory Suggestions' Booklet

During recent months, the J. T. Baker Chem. Co. has mailed a 12-page compilation of laboratory suggestions to over 20,000 chemists in the United States. All of these suggestions originally appeared in the CHEMIST-ANALYST during the period 1949-1954. Only a limited supply of this booklet remains. If you have not received a copy and have not maintained a file of this journal throughout this period, a copy will be sent to you upon request. Write— J. T. Baker Chemical Co., Dept. R-V, Phillipsburg, N. J.

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". . . words, words, words . . ."

This issue contains more words of technical copy than any previous issue of CHEMIST-ANALYST during the 44 years of its existence. To maintain this gristmill for words at the present level, the Editors urge the readers to continue submitting contributions at the current high rate.

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